

GENERATION OF CHARGE CARRIERS IN ANTHRACENE
WITH POLARIZED LIGHT

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Intrinsic photogeneration of charge carriers in anthracene single crystals occurs with photon energies in excess of 4 eV^{1-4} . The mechanism of this process, however, is not well understood. The interpretation of the wavelength dependence of this current in particular is difficult.² Two maxima in the photocurrent appear, one at $4.4 \text{ eV}^{1,2,4}$ and the other at 5.4 eV^2 . The 4.4 eV maximum appears in a region of low absorption coefficient ($k \sim 16,000 \text{ cm}^{-1}$) and the other maximum in wavelength region where $k \sim 113,000 \text{ cm}^{-1}$. It has been proposed that bulk generation of carriers in anthracene proceeds by direct excitation into a conduction band. On this basis an inverse dependence on k of the bulk generated photocurrent was predicted,^{4,5} which seems to explain the wavelength dependence of the 4.4 eV maximum,⁵ but not that of the 5.4 eV peak.² In order to ascertain the dependence of the bulk generated photocurrent on k we studied the relative quantum efficiency of the photocurrent at fixed wavelength as a function of the angle θ between the electric vector of the polarized light and the b crystalline axis. The extent of variation of k with θ depends on the wavelength,⁶ being

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largest at $37,300 \text{ cm}^{-1}$ in the wavelength region of interest to us ($32,000 - 46,000 \text{ cm}^{-1}$). The bulk generated current, designated by i^- , was measured in a sandwich arrangement with water electrodes with the illuminated side of the crystal at a negative potential (i^+ is the photocurrent with the illuminated side at a positive potential and is mostly due to an extrinsic surface generation of carriers^{2,7}). Studies of i^+ and i^- as a function of k usually involve changing the excitation wavelength; this simultaneous change of photon energy as well as of k , introduces an uncertainty in the interpretation of the results. However, by using polarized light, k can be varied conveniently by changing θ , whereas the photon energy remains constant. In our experiments the exciting light was polarized by means of a Glan-Taylor prism. Both i^+ and i^- were studied as a function of θ at different wavelengths in the range indicated above. The results at $37,300 \text{ cm}^{-1}$ (4.6 eV where maximum variation of k with θ occurs) are shown in figure 1. $k(\theta)$ was calculated from the data of Lyons and Morris⁶ who give values of the molar extinction coefficient ϵ parallel to the b and a crystalline axes. Using $k = 2.303 \epsilon c$ ($c = 7.0 \text{ mol l}^{-1}$, molar concentration of solid anthracene), the expression $k(\theta) = k_b \cos^2 \theta + k_a \sin^2 \theta$ was used to calculate $k(\theta)$, where k_b and k_a are the absorption coefficients parallel to the b and a axes respectively.

Since i^+ depends on a diffusion of excitons to the surface where they dissociate,^{2,7} this current is a strong function of $k(\theta)$. i^- , however, which is a bulk generated current is fairly

independent of k (θ). This is also the case for the entire wavelength range investigated and has been verified for eight other crystal surfaces, the variation never exceeding $\pm 10\%$ at any wavelength. It is conceivable that triplet excitons with a long diffusion length could reach the back side of the crystal to produce hole injection. This would be an i^- current independent of θ , but would exhibit all the characteristics of the extrinsic i^+ current. Such a process should therefore saturate with voltage⁸, which is not observed.² This possibility can therefore be ruled out.

It is evident from these results that the wavelength dependence of i^- cannot be attributed to a dependence on k^{-1} as proposed by other workers.^{4,5} We shall now restate the two possible mechanisms for intrinsic carrier generation² and attempt to distinguish the most probable one in view of our present findings.

I. Direct band to band (BB) transition,^{4,5} characterized by an absorption coefficient α (cm^{-1}).

II. Autoionization (AI)^{7,2} - light absorption of appropriate energy generates excited bound molecular states which have sufficient energy to ionize, the probability being ϕ . The absorption coefficient for the autoionization state is $k^i \text{ cm}^{-1}$; the total absorption coefficient for a crystal is thus $k = k^i + \alpha$. AI, however, may not necessarily lead to free carrier formation where the electron is free of the coulomb field of its parent ion.⁷ The mean free path

of the electron may be so small⁹ that the kinetic energy of the electron is degraded before it can escape, leading to its re-capture by the parent ion⁷ (first-order recombination); a re-combination between free holes and electrons is second-order. When the electron and hole densities are comparable, the latter implies that the photocurrent depends on the square-root of the light intensity I_0 as long as the photocurrent is field dependent. We observe, however, that i^- depends linearly on I_0 although it is also field dependent.² Furthermore, second-order recombination is ruled out by the low carrier densities in our experiments,⁷ (10^5 - 10^6 cm⁻³).

AI may produce quasi-free electron states from which free carriers are produced subsequently under the influence of temperature T or applied field E with probability $\gamma(E,T)$. The effect of E on carrier generation has been proposed by us for tetracene⁷ and by other workers for anthracene.¹⁰ If free carriers are not formed, the quasi-free electron state decays via the charge-transfer exciton state observed by Pope and Burgos,³ in which the hole and electron are on adjacent molecules.

A consideration of steady state kinetics of formation of free carriers and their disappearance at the electrode in absence of second-order recombination, leads to the following expression for i^- :

$$i^- = \frac{e I_0}{k} \gamma(E,T) [\alpha + \phi k'] \quad (1)$$

Both generation mechanisms (BB) and (AI) have been assumed with the generalization that quasi-free electron states may also be formed by the BB mechanism⁹ in which case α must also be multiplied by $\gamma(E,T)$. e is the electronic charge. We shall now examine mechanisms I and II in context of equation (1). If BB transitions prevail over the AI transition, $\alpha \gg \phi k'$ and i^- should vary as k^{-1} unless $\alpha \propto k \approx k$. The latter would imply that absorption of light in anthracene occurs mostly to crystal continuum states. A detailed interpretation of the anthracene crystal spectrum by Lyons and Morris,⁶ however, shows that it can be explained in terms of excited electronic states of the anthracene molecule. Even if $\alpha \propto k$, it is highly unlikely that $\frac{\alpha}{k}(\theta)$ is a constant at all wavelengths which would have to be the case to explain the θ independence of i^- .

It thus appears that the experimental facts can be much better described by the AI than by the BB mechanism. In this case i^- is proportional to $\gamma(E,T) \phi k'/k$; $\gamma(E,T)\phi$ determines the quantum efficiency of intrinsic carrier generation and $k' \approx k$, thus satisfying the experimental requirement that i^- is independent of $k(\theta)$. We further conclude that an inverse dependence of the photocurrent on k is not a criterion for bulk generation as proposed by Chaiken and Kearns.⁴

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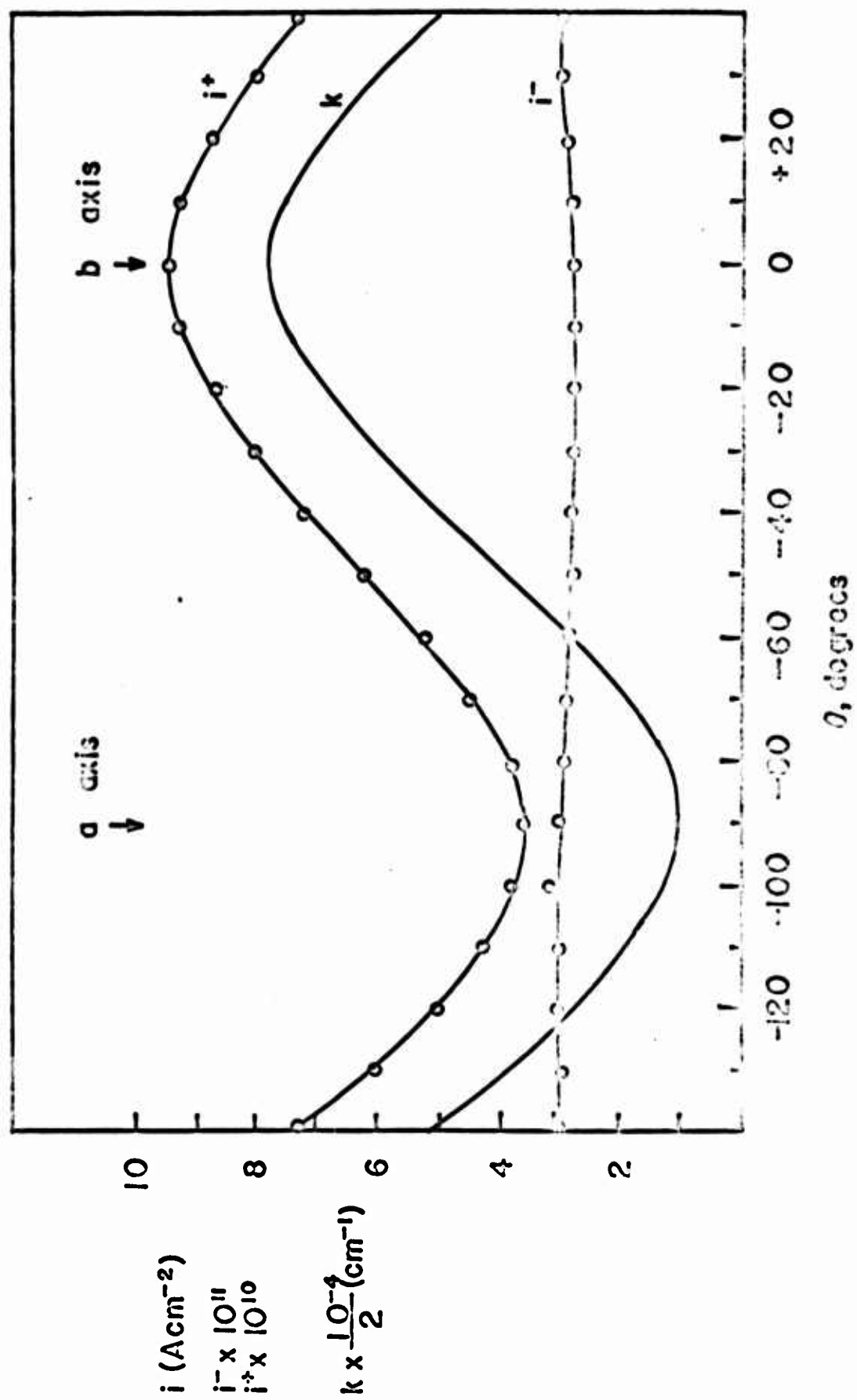


FIGURE 1. Photocurrents in anthracene single crystal (35 microns thick) and absorption coefficient k as function of angle θ between electric vector of exciting polarized light and b crystal axis. Wavelength corresponds to photon energy of 4.6 eV ($37,300 \text{ cm}^{-1}$). Light intensity $1.5 \times 10^{11} \text{ quanta cm}^{-2} \text{ sec}^{-1}$, field intensity 40,000 volts cm^{-1}